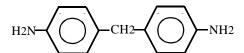
4,4-METHYLENEDIANILINE

4,4-Methylenedianiline is a federal hazardous air pollutant and was identified as a toxic air contaminant in April 1993 under AB 2728.

CAS Registry Number: 101-77-9

Molecular Formula: $C_{13}H_{14}N_2$



4,4-Methylenedianiline is a light brown crystalline solid with a faint amine odor. It is slightly soluble in water and soluble in alcohol, benzene, and ether. It is also combustible when exposed to heat or flame. When heated to decomposition, it emits toxic fumes of aniline and oxides of nitrogen (NTP, 1991).

Physical Properties of 4,4-Methylenedianiline

Synonyms: p,p-diaminodiphenylmethane; 4,4-methylenebis[benzenamine];

4-(4-aminobenzyl)aniline

Molecular Weight: 198.26

Boiling Point: 398 - 399 °C at 768 mm Hg

Melting Point: 91.5 - 92 $^{\circ}$ C Flash Point: 226 $^{\circ}$ C (440 $^{\circ}$ F) Conversion Factor: 1 ppm = 8.1 mg/m³

(Merck, 1983; Sax, 1987; U.S. EPA, 1994a)

SOURCES AND EMISSIONS

A. Sources

4,4-Methylenedianiline is used for determination of tungsten and sulfates, as a polymer and dye intermediate, as a corrosion inhibitor, as an epoxy resin hardening agent, in isocyanate resins, and in polyamides (Sax, 1987). The primary stationary sources that have reported emissions of 4,4-methylenedianiline in California are manufacturers of aircraft and parts, manufacturers of electronic components and accessories, and manufacturers of miscellaneous textile goods (ARB, 1997b).

B. Emissions

The total emissions of 4,4-methylenedianiline from stationary sources in California are estimated to be at least 1,400 pounds per year, based on data reported under the Air Toxics "Hot Spots" Program (AB 2588) (ARB, 1997b).

C. Natural Occurrence

4,4-Methylenedianiline is not known to occur as a natural product (HSDB, 1991).

AMBIENT CONCENTRATIONS

No Air Resources Board data exist for ambient measurements of 4,4-methylenedianiline.

INDOOR SOURCES AND CONCENTRATIONS

No information about the indoor sources and concentrations of 4,4-methylenedianiline was found in the readily-available literature.

ATMOSPHERIC PERSISTENCE

4,4-Methylenedianiline may be expected to partition between the gas and particle phases, and rapid wall-losses have been observed in environmental chambers (Becker et al., 1988). Based on the appropriate rate constant measured by Becker et al. (1988) for gas-phase reaction of 4,4-methylenedianiline with photochemically produced hydroxyl radicals, the half-life for gaseous 4,4-methylenedianiline is estimated to be 0.3 days (Atkinson, 1995). Crystalline forms in the atmosphere are susceptible to oxidation in the presence of air and light. Physical removal of these particulates from air may occur through washout and dry deposition (HSDB, 1991).

AB 2588 RISK ASSESSMENT INFORMATION

The Office of Environmental Health Hazard Assessment reviews risk assessments submitted under the Air Toxics "Hot Spots" Program. 4,4-Methylenedianiline contributed to the total cancer risk in 1 of the approximately 550 risk assessments reporting a total cancer risk equal to or greater than 1 in 1 million. 4,4-Methylenedianiline also contributed to the total cancer risk in 1 of the approximately 130 risk assessments reporting a total cancer risk equal to or greater than 10 in 1 million (OEHHA, 1996a).

For non-cancer effects, 4,4-methylenedianiline did not contribute to a total hazard index greater than 1 in any of the risk assessments reporting a total chronic or acute hazard index greater than 1 (OEHHA, 1996b).

HEALTH EFFECTS

Probable routes of human exposure to 4,4-methylenedianiline are inhalation, ingestion, and dermal contact (U.S. EPA, 1994a).

Non-Cancer: 4,4-Methylenedianiline is highly hepatotoxic. A single large exposure or repeated smaller exposures can cause serious liver disease (toxic hepatitis) with symptoms of fever, upper abdominal pain, jaundice, and loss of appetite. Exposure can also irritate the eyes and skin, and cause methemoglobinemia. From animal studies in which rats and mice were chronically exposed to 4,4-methylenedianiline in their diets, lesions of the thyroid and liver, mineralization within the kidneys, and reduced body weight gain were observed (U.S. EPA, 1994a).

A chronic non-cancer Reference Exposure Level (REL) of 1.9 micrograms per cubic meter (μ g/m³) is listed for 4,4-methylenedianiline in the California Air Pollution Control Officers Association Air Toxics "Hot Spots" Program, Revised 1992 Risk Assessment Guidelines. The toxicological endpoints considered for chronic toxicity are the gastrointestinal system and liver (CAPCOA, 1993). The Reference Concentration (RfC) for 4,4-methylenedianiline is under review by the United States Environmental Protection Agency (U.S. EPA). An oral Reference Dose (RfD) has not been established (U.S. EPA, 1994a).

No information is available on adverse developmental or reproductive effects of 4,4-methylenedianiline in humans or animals (U.S. EPA, 1994a).

Cancer: No information is available on the carcinogenic effects of 4,4-methylenedianiline in humans. In rats and mice exposed to 4,4-methylenedianiline dihydrochloride in drinking water, significant increases in several tumor types, including liver and thyroid, were reported. The U.S. EPA has not classified 4,4-methylendianiline for carcinogenicity (U.S. EPA, 1994a). The International Agency for Research on Cancer (IARC) has classified 4,4-methylenedianiline in Group 2B: Possible human carcinogen (IARC, 1987a).

The State of California under Proposition 65 has determined that 4,4- methylenedianiline (4,4'-diaminodiphenylmethane) is a carcinogen (CCR, 1996). The inhalation potency factor that has been used as a basis for regulatory action in California is 4.6×10^{-4} (microgram per cubic meter)⁻¹ (OEHHA, 1994). In other words, the potential excess cancer risk for a person exposed over a lifetime to $1 \mu g/m^3$ of 4,4- methylendianiline is estimated to be no greater than 460 in 1 million. The oral potency factor that has been used as a basis for regulatory action in California is 1.6 (milligram per kilogram per day)⁻¹ (OEHHA, 1994).